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DRAFT: A MACROSCOPIC MODEL OF THE THERMO-CHEMO-MECHANICAL BEHAVIOUR OF MIXED IONIC AND ELECTRONIC CONDUCTORS

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ABSTRACT

This paper suggests a macroscopic model describing the thermo-chemo-mechanical behaviour of ceramic dense membrane for oxygen separation application. This work takes in account to oxygen permeation and strain induced by stoichiometry variation with working conditions. This model, developed within the traditional framework of phenomenological approach, is based on the assumption of strain partitions and requires only three state variables: oxygen activity, temperature and total strain. Oxygen bulk diffusion and surface exchanges are described thanks to the Onsager approach. While many works focused on semi-permeation induced strain, the proposed model also includes the temperature effect on chemical expansion. Strains predicted by the proposed model are validated thanks to experimental test on $La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-\delta}$. *Implemented in F.E.A code Abaqus, this model permits studying the design and the process management effects on the membrane reliability.*

NOMENCLATURE

a	Oxygen activity
a_s	Surface oxygen activity
α	Coefficient of thermal expansion
α_c	Thermal chemical expansion coefficient
β	Chemical expansion coefficient
D_0	"intrinsic" oxygen diffusivity
$\boldsymbol{\varepsilon}$	Total strain tensor
$\boldsymbol{\varepsilon_c}$	Chemical strain
ε_c^T	Chemical strain induce by the temperature change
ε_c^{max}	Maximum chemical strain amplitude
$\boldsymbol{\varepsilon_e}$	Elastic strain
$\boldsymbol{\varepsilon_T}$	Thermal strain
$\boldsymbol{I}$	Second rank identity tensor
$\boldsymbol{J_b}$	Bluk density of oxygen flux
$\boldsymbol{J_s}$	Oxygen flux through surfaces
k	Surface exchange coefficient
$\boldsymbol{K}$	Four rank Hooke tensor
$\boldsymbol{n}$	Normal vector
P_{O_2}	Partial oxygen pressure
P_{ref}	Oxygen partial pressure corresponding to chemical strain equal to zero
Q	Activation energy
R	Ideal gas constant
$\boldsymbol{\sigma}$	Second rank stress tensor
T_0	Reference temperature
$T^{\times}$	Temperature of activation of chemical strain induce by the temperature change

INTRODUCTION

Since more than twenty years, Mixed Ionic and Electronic Conductors (MIECs) are promising membrane materials for the pure oxygen production which have potential industrial applications like methane reforming or oxycombustion [1]. These technologies consist in oxygen separating from air using a dense ceramic membrane through the oxygen bulk diffusion at high temperature under a gradient of oxygen partial pressure.

Two fundamental key points for their development are lifespan and reliability of the membrane. The first point is mainly driven by material stability under operating conditions, whereas the second point is directly linked to mechanical stress induced by the chemical expansion of MIECs in working conditions. Most of the works focus on material properties such as, a high permeation rate and a good stability, but few study deals with mechanical reliability of membranes [2].

The development of a macroscopic model of MIECs materials dedicated to engineering design department is necessary to investigate the reliability in service. This macroscopic model describes the thermo-chemo-mechanical behaviour of MIECs to take in account to oxygen permeation, thermal expansion and strain induced by the stoichiometry fluctuation in working conditions. The previous models had focused on semi-permeation induced strain [3], the current model also includes the temperature effect on chemical expansion due to the defect equilibrium dependence to temperature. To test this model, strains predicted are compared with the measured strains for the particular case of $La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-\delta}$.

Finally, the implementation of this model in the F.E.A code Abaqus permits the investigation of the stress state of tubular membrane for syngas production taking into account the residual stress induced by each stages from sintering, sealing to in-service loadings.

SEMI-PERMEATION MODEL

The oxygen bulk diffusion can be model using the Onsager approach, developed for MIECs by Wagner [4], which leads to the local expression of the bulk density $\boldsymbol{J_b}$ of oxygen flux:

$$\boldsymbol{J_b} = D_0 e^{-Q/RT} \boldsymbol{grad}|_T(\ln a) \tag{1}$$

Where a is the oxygen activity, D0 the "intrinsic" oxygen diffusivity, Q the activation energy, R the ideal gas constant and T the temperature in Kelvin. For LSFG, value of D0 =100 m2.s-1 and Q=138 kJ.mol^{-1} have been estimated by inverse identification. The extension of this approach to surface exchanges, as proposed by Fer [5] leads to:

$$\boldsymbol{J_s} = k\ln\left(\frac{a_s}{P_{O2}}\right)\mathbf{n} \tag{2}$$

Where $\boldsymbol{J_s}$ is oxygen flux through surfaces and k is the surface exchange coefficient.

THERMO-CHEMO-MECHANICAL BEHAVIOUR

In working condition, the stresses in the membrane are mainly due to the "chemical strain" gradient which is induced by the stoichiometry fluctuation related to oxygen bulk diffusion. The macroscopic model describing the thermo-chemo-mechanical is based on the assumption of small strain partitions:

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon_T} + \boldsymbol{\varepsilon_e} + \boldsymbol{\varepsilon_c} \tag{5}$$

Where $\boldsymbol{\varepsilon}$ is the strain second rank tensor, $\boldsymbol{\varepsilon_T}$ the thermal strain second rank tensor, $\boldsymbol{\varepsilon_e}$ the elastic strain second rank tensor and $\boldsymbol{\varepsilon_c}$ the chemical strain second rank tensor. In the following text, bold type refers to tensor, while normal type refers to scalar. The assumption of elastic behaviour leads to:

$$\boldsymbol{\sigma} = \boldsymbol{K}:\boldsymbol{\varepsilon_e} \tag{6}$$

Where $\boldsymbol{K}$ is the four rank Hooke tensor and $\boldsymbol{\sigma}$ the second rank stress tensor. The thermal strain tensor depends on temperature variation in a reversible way:

$$\boldsymbol{\varepsilon_T} = \alpha(T - T_0)\mathbf{I} \tag{7}$$

Where α is the coefficient of thermal expansion, T_0 a reference temperature and $\mathbf{I}$ the second rank identity tensor. The thermal deformation corresponds here exclusively to the deformation caused by temperature variation at constant composition and without any phase change.

The chemical strain is due to the oxidation state (linked to the stoechiometry) of the material. For a constant temperature, the oxidation state is driven by the oxygen partial pressure of the atmosphere, whereas at constant oxygen partial pressure the oxidation state is driven by the temperature. Then, a macroscopic model of the chemical expansion behaviour should take into account the effect of temperature and oxygen partial pressure.

The first assumption of the proposed model is the reversible dependence of the chemical strain with oxygen partial pressure variation. This assumption has been previously validated by isothermal expansion and XRD measurement under different atmospheres on different MIECs [6]. The second assumption is that, thanks to the admissible degree of oxidation fluctuation, in accordance with material stoichiometry, the temperature drives the intensity of the chemical expansion induced by the atmosphere change. Then, it leads to:

$$\varepsilon_c = \beta\ln\left(\frac{P_{O_2}}{P_{ref}}\right) + \varepsilon_c^T \leq \varepsilon_c^{max} \tag{8}$$

The first term of Eqn. (8) corresponds to the part of the chemical expansion induced by the atmosphere change, in agreement with the previously proposed expression [7]. In this term, β is the chemical expansion coefficient, P_{O2} the current oxygen partial pressure and P_{ref} the oxygen partial pressure corresponding to chemical strain equal to zero. The second part ε_c^T, represent the chemical strain induced by the temperature change. The latest term ε_c^{max} , is the maximum chemical strain amplitude which corresponds to the larger acceptable stoichiometry fluctuation for the considered material. In a first approximation, let us proposed a linear expression for the thermal effect on chemical expansion:

$$\varepsilon_c^T = \alpha_c\langle T - T^{\times}\rangle \tag{9}$$

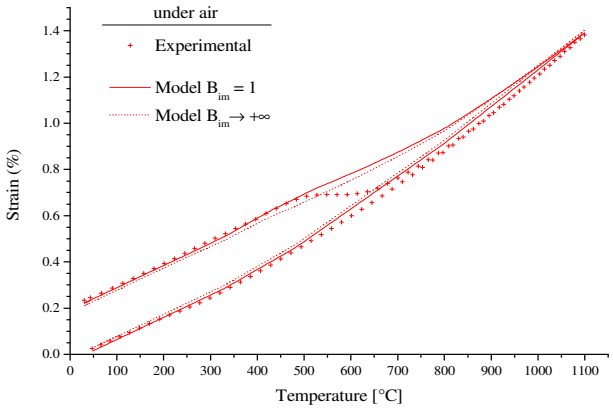

FIGURE 1: THERMAL AND CHEMICAL EXPANSION UNDER AIR FOR LSFG INITIALLY STABILIZED UNDER NITROGEN (STARTING POINT AT 0.2% OF STRAIN AT RT).

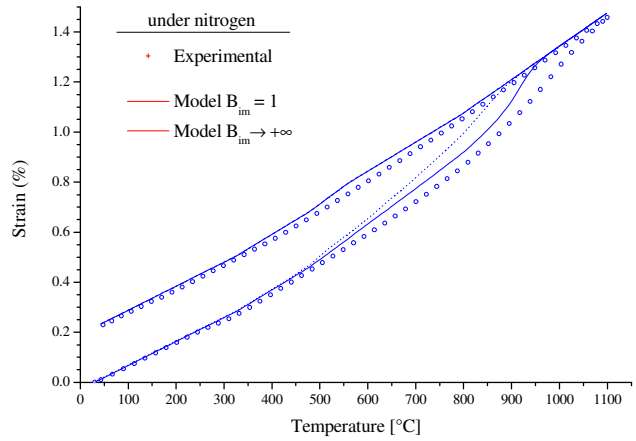

FIGURE 2: THERMAL AND CHEMICAL EXPANSION UNDER NITROGEN FOR LSFG SINTERING UNDER AIR.

Where α_c is the thermal chemical expansion coefficient, $T^{\times}$ is the temperature of activation of this effect and $\langle x \rangle$ is the positive part of x.

The identification of $\alpha_c, \beta, T^{\times}, \varepsilon_c^{max}$ requires cyclic thermal expansion test with atmosphere change between each cycles[16]. For LSFG, the obtained values are: $\alpha_c = 2.5\ 10^{-6} K^{-1}$, $\beta = -2.10^{-4}$, $T^{\times} = 500°C$, $\varepsilon_c^{max} = 0.25\%$.

NUMERICAL SIMULATIONS

The mechanical behaviour accounting for the chemical strain (8), the oxygen bulk diffusion behaviour (1) and the surface exchanges (2) have been implemented in the finite element code Abaqus thanks to user subroutines.

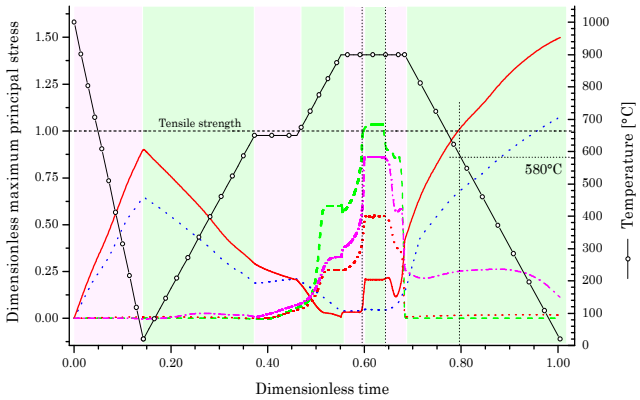

FIGURE 3: EVOLUTION OF DIMENSIONLESS MAXIMUM PRINCIPAL STRESS AT DIFFERENT LOCALIZATION ALONG THE MEMBRANE LIFE.

Figures 1 and 2 show the comparison between experimental results of thermal expansion test under atmosphere and numerical prevision. The strain amplitude is quite good whereas the kinetic does not fit the curves. Kinetics seem too fast under air and too slow under nitrogen. It underlines that the simplified semi-permeation model used here need to be refined.

However, considering only the case of stationary states, the chemical strain is quantitatively good. Then, it allows to use the model to estimate the mechanical stress induced by stoichiometry change in stationary state.

To illustrate the possibility offered by such macroscopic model, the case of a tubular membrane of LSFG, close at one end, has been studied. After sintering, the membrane is sealed at its bottom. This process generates mechanical stress that can damage the tube. Then, the membrane is set in the methane reforming reactor to produce syngas. Feed air arrives inside, while methane flow is at the outside face. Before reaching the steady production conditions in term of atmosphere, temperature and flow rates, intermediate steps are needed. Then, after a reasonable production time, the reactor may need to be stopped. Each step has an impact on the stress field and on the following step. Then, all the solicitations have to be computed accounting for the cycle process.

Figure 3 shows the evolution of the maximal principal stress at different localizations in the membrane. The red line describes stress evolution near the sealing, the green one near the closed on the top of the membrane and other colors correspond to intermediate levels. Firstly, it is assumed that the membrane is stress free at the beginning of the cooling of the sealing under air. Consequently, after cooling, the thermal expansion coefficient mismatch between LSFG, sealing material and steel, combine to the geometry of the sealing, produce high stress intensity close to the tensile strength. After being installed in the reactor, the start up procedure is applied. The heating up is realized under inert atmosphere to relax stresses. Then both atmospheres are switched to respectively air

on inner face and methane on outer face. This induces high mechanical solicitations, but stresses remains below membrane strength. Finally, the specific case of a safety shut down of the reactor has been simulated. It appears that it can lead to the breakage of the membrane.

CONCLUSIONS

The macroscopic model briefly summarized in this paper has been developed to study the effect of reactor design and management on mechanical reliability of the membrane. The temperature and the partial pressure have been deliberately chosen as state variables because they can be "easily" measured and managed in service. The results show that, whereas the chemical expansion is well reproduced, the surface exchange kinetics need to be refined. However, the model permits to quantify the mechanical stresses in the membrane under steady-state service conditions, accounting for geometry and mechanical design of each part of the reactor. Such macroscopic model dedicated to mechanical engineering of MIECs should provide an help to the development of industrial application and of these promising materials.

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